

Princeton University  
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TRIBOLUMINESCENCE AND LIGHT AT  
DEEP SEA HYDROTHERMAL VENTS

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## Triboluminescence and Light at Deep Sea Hydrothermal Vents

"In considering the light seen at the vent orifice it is likely that we have been overly simplistic and the situation is more complex than can be explained in terms of laboratory experience with crystallo, sono, etc. luminescence, or even a combination of these. The situation is much more complex, involving the shear interface of a very hot (and sometimes maybe even supercritical) water plume containing a variety of elements, gases and dissolved compounds emerging at high speed (100 cm/sec) into distinctly cooler sea water under high pressure. At the shear interface we may have a kind of "liquid triboluminescence" involving charge separation or excited states. It may be a liquid analogue of frictional electricity. There may be crystalloluminescence, there may be sonoluminescence, but caused in, or enhanced by gas liquid interfaces and due to Bernoulli flow induced cavitation. Certainly at longer wavelengths we can expect to find characteristic thermal radiation. It is at the shorter wave lengths (visible) that light inconsistent with thermal, light seen by CCD's and photodetectors is of interest to investigate for evidence of complex physical phenomena. If it has a significant surface component the images might in favorable symmetries of orifice geometry show an intensity profile assuming the emission is not lambertian.

In view of the cost of an expedition and individual dives, it is not unreasonable to suggest a laboratory experiment. The pressures are not excessive, the temperatures are moderate, the plume velocities are reasonable. It should be possible to send "sea water" containing iron sulfides, manganese compounds etc. through a mock up vent and view with a CCD. We have seen evidence for sodium radiation ( $\sim 500$  nm) and an occasional hint of radiation  $\sim 800$  nm. Potassium and sulfur ions have emissions in the range 750-950 nm. Excitation mechanisms at the shear interface are distinctly possible." [1]

Although a completely realistic mock up vent experiment has not been made, several elementary laboratory experiments have yielded suggestive results. One of these has already been reported. [2] There is extensive literature on the structure and components of the chimneys associated with vents. [3-13] These studies, combined with analyses of particles recovered from the plumes of the "black smokers" (performed by the authors of the cited papers), suggest a simple laboratory experiment.

The main minerals found in chimney structures include:

Sphalerite,  $\text{ZnS}$ ; tetrahedral

Wurtzite,  $\text{ZnS}$ ; hexagonal

Pyrite,  $\text{FeS}_2$

Pyrohotite,  $\text{FeS}$  or  $\text{Fe}_{1-x}\text{S}_x$

Cubanite,  $\text{CuFe}_2\text{S}_3$

Bornite,  $\text{Cu}_5\text{FeS}_4$

Manganite,  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Chalcopyrite,  $\text{CuFeS}_2$

As a class iron, copper, zinc, sulphides are known to be triboluminescent. [14,15] Samples of these minerals have been obtained from Ward's Geology Supply\* in the form of "Testing Chips". The individual chips are probably not pure (not represented as research grade) but are suitable as representative of vent and plume minerals. They were tested using an RCA 8575 photomultiplier, Kiethley 606 Electrometer whose output was recorded on a Soltec chart recorder.

The capability of the system to record the light signal from the triboluminescence of the various minerals was confirmed by fracturing them. Typical results are shown in Figs. 1-3.

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\*Ward's, PO Box 92912, Rochester, NY 14692-9012.

Further observation of triboluminescence was based on consideration that these materials are found in the plumes of "black smokers". These plumes are well known to be turbulent, both from video records obtained in Alvin dives, and from evidence of the fluctuating visible light recorded by Aliss in a dive at the Jan de Fuca Ridge. [16] Although this turbulence is more severe than can easily be achieved in the laboratory, and also at higher temperatures, temperature gradients, and pressures, a simple experiment was performed to explore the possibility that particles such as those found in plumes might emit light upon collision with each other. To test, a small sample of crushed material was placed in tap water at room temperature. This sample was placed in a glass beaker (100 ml) positioned over the cathode of the photomultiplier, and stirred with a glass rod. Light signals were observed, samples of which are shown in Figures 4 and 5 (control exposures stirring with no minerals in the water, gave no signal).

The nature of the minerals found in chimneys, presumably deposited by precipitation from the vent fluid, and the minerals found as particles in the black smoker plumes, suggest a combination of light producing phenomena that may make a major contribution to the light seen at the vent orifices: crystalloluminescence within the vent, triboluminescence outside the vent. Until recently, the main focus has been on crystalloluminescence outside the vent, and this might be a contributing source, but clearly triboluminescence must also receive consideration. Crystalloluminescence within the vent might be an intense source, the light from which could be (Mie) scattered outside the vent by plume particles, which are themselves exhibiting triboluminescence.

This hypothesis could be required to meet two constraints: spectral analysis of the light, compared to crystallo- and triboluminescence spectra of the minerals considered, and the spatial distribution of the light in the vertical direction of the plumes. As far as the sensitivity of the present detectors indicate, the light is concentrated close to the orifice. Presumably turbulence continues to some degree as the plume rises, and particles continue to collide. However, temperatures drop drastically away from the orifice, and mixing with sea water occurs rapidly, decreasing the concentration of particles and thus the frequency of

collisions. Also, there is reason to believe that the turbulence at the orifice is much greater than that existing even 10 or 20 centimeters away.

There still remain the complex possibilities of chemiluminescence and vapor bubble luminescence to be more thoroughly investigated, but simple experiments show that crystal-luminescence, triboluminescence, turbulence, and light scattering are reasonable sources for the observed light.

In view of the presence of ZnS in chimneys and plumes it was of interest to investigate the response to pressure of a sample of ZnS deposited on mylar, which was used as a scintillator to convert x-rays to visible lights in early x-ray diffraction studies. [17,18] ZnS(Ag) was deposited to a thickness of  $13 \text{ mg/cm}^2$  (about  $80 \text{ }\mu\text{m}$  thick). When this sample was subjected to a very slight pressure, the photomultiplier signal was much stronger than those of the minerals tested (Fig. 6).

#### Acknowledgements

GTR benefited from helpful discussions with Rachel Haymon, Meg Tivey, Karen Von Damm and Richard Feely.

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## Figure Captions

**Figure 1** Photomultiplier response of a Sphalerite chip subjected to light taps, resulting in fracture. The sharp initial positive spike is the result of the pm voltage turn on. The final negative spike occurs when the voltage is turned off.

**Figure 2** Response of Chalcopyrite chip to light taps, resulting in fracture.

**Figure 3** a) Response of Bornite chip.

b) Control.

**Figure 4** a) Response of a number of small particles of Sphalerite in water, stirred with a glass rod.

b) Control.

**Figure 5** Response of Chalcopyrite to stirring.

a) Control.

b) Small particles.

c) Larger chip added.

**Figure 6** Response of ZnS(Ag) to very light finger pressure.

a) Chart paper not in motion.

b) Chart paper in motion as in Figs. 1-5.



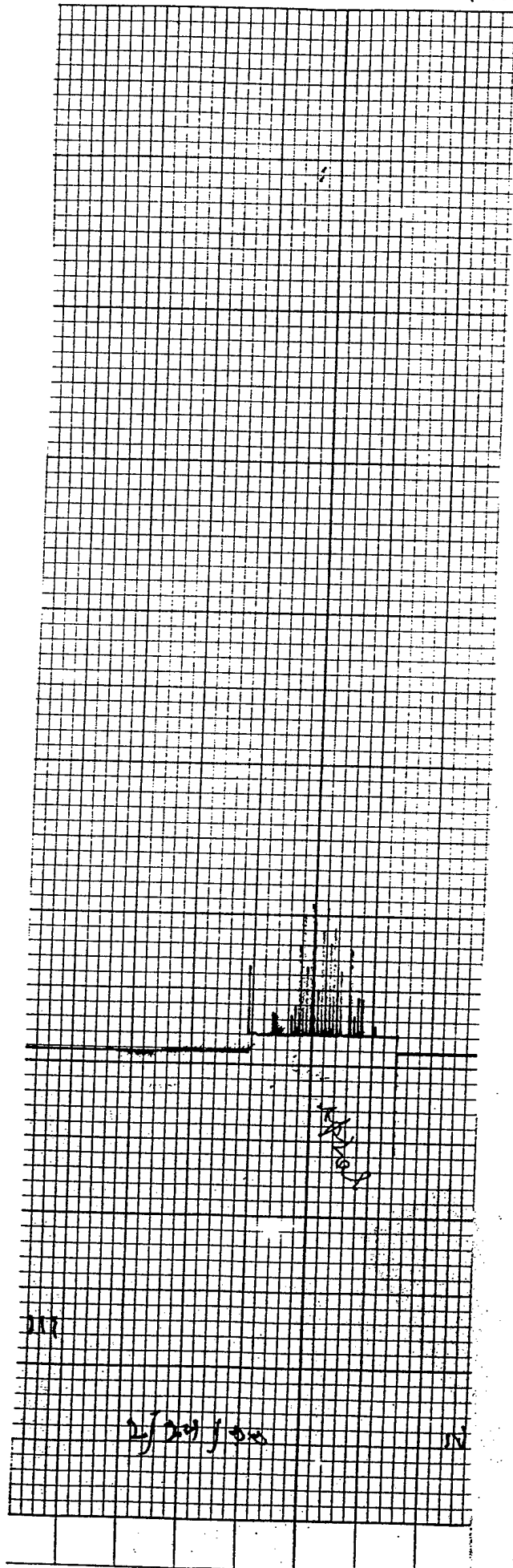


Figure 1

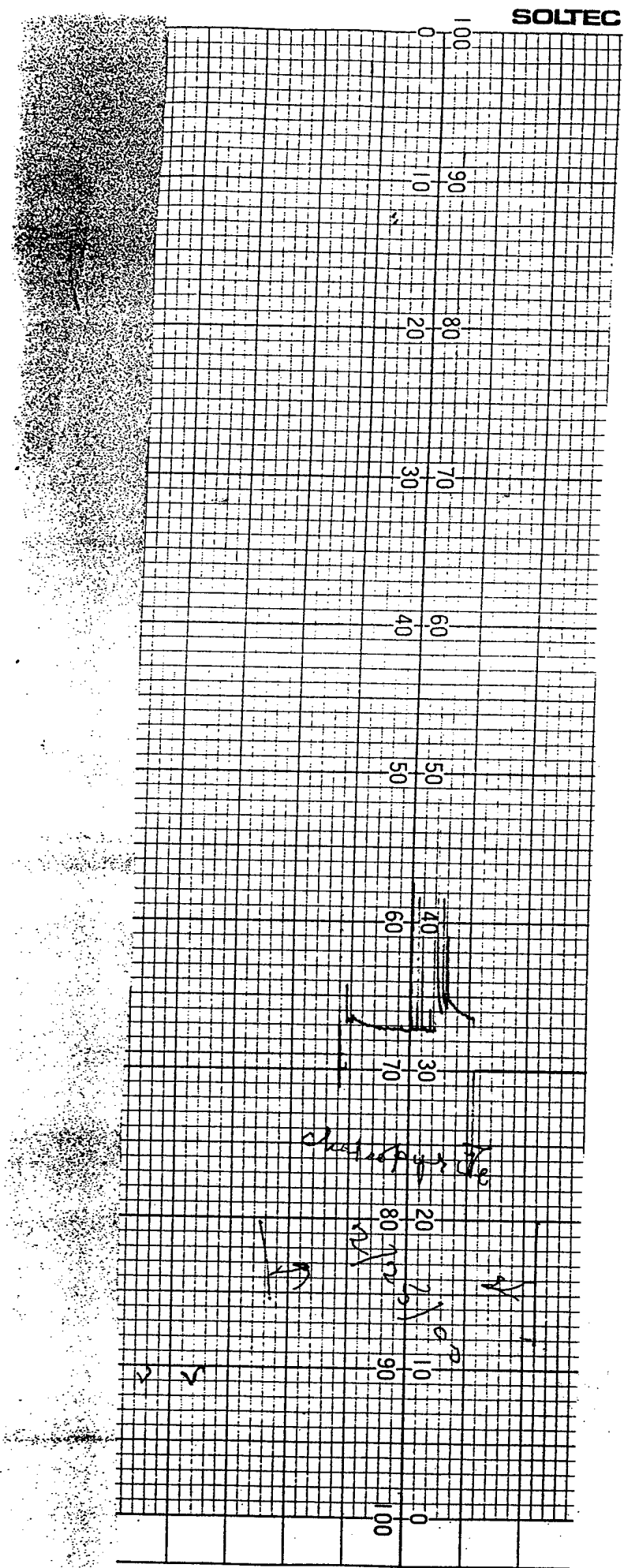


Figure 2

Figure 3a

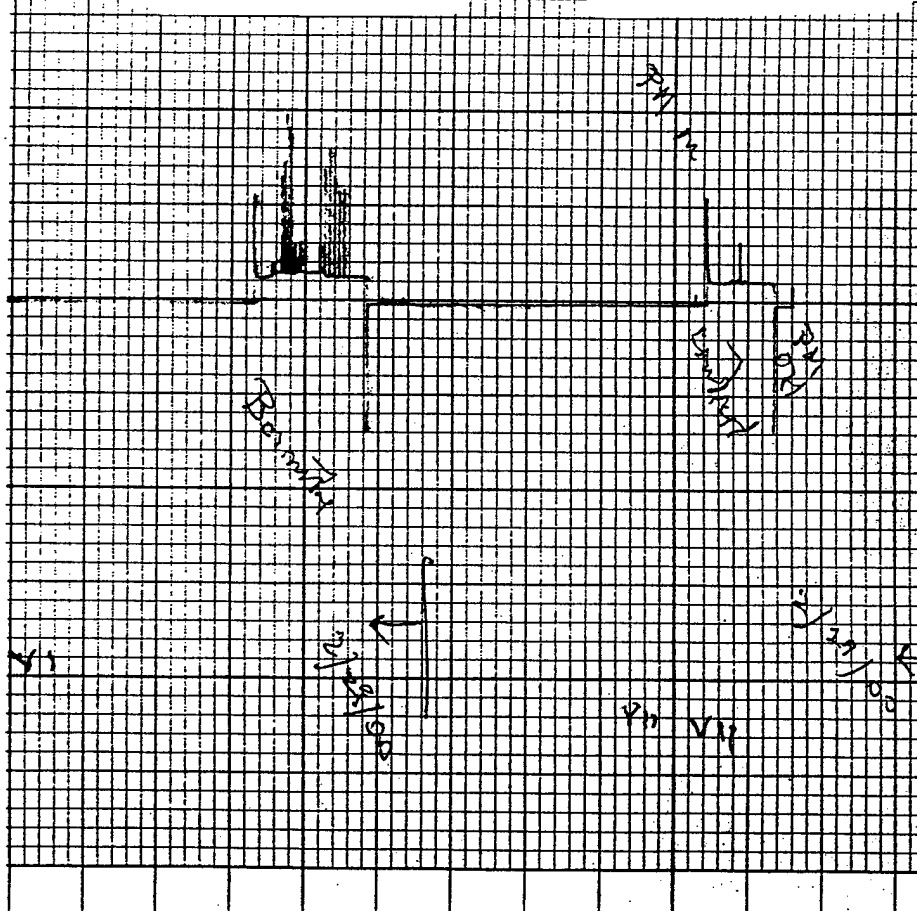


Figure 3b

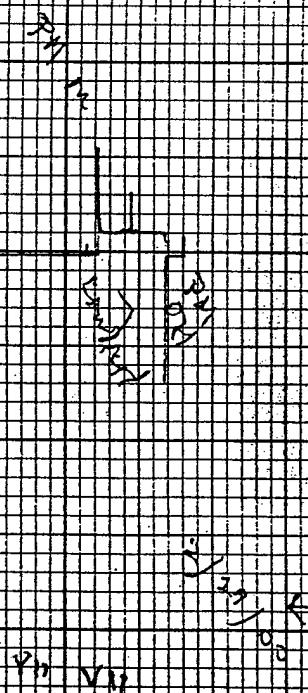
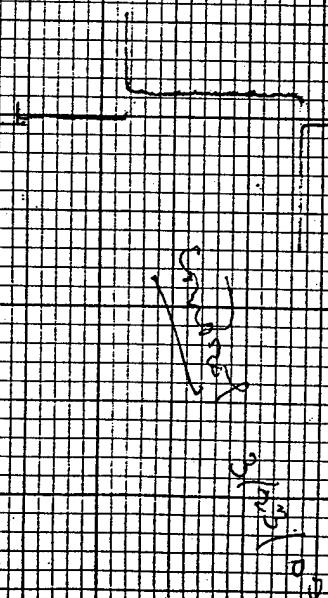
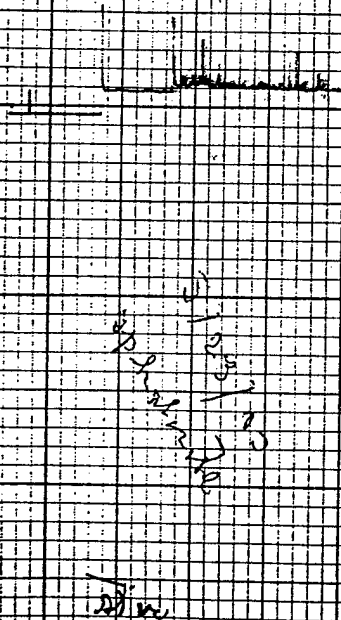


Figure 4a

Figure 4b



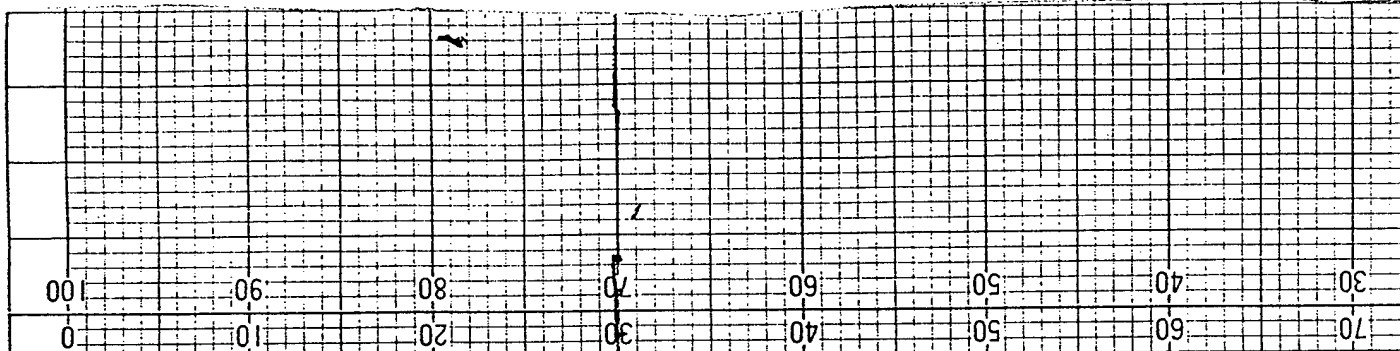


Figure 5a

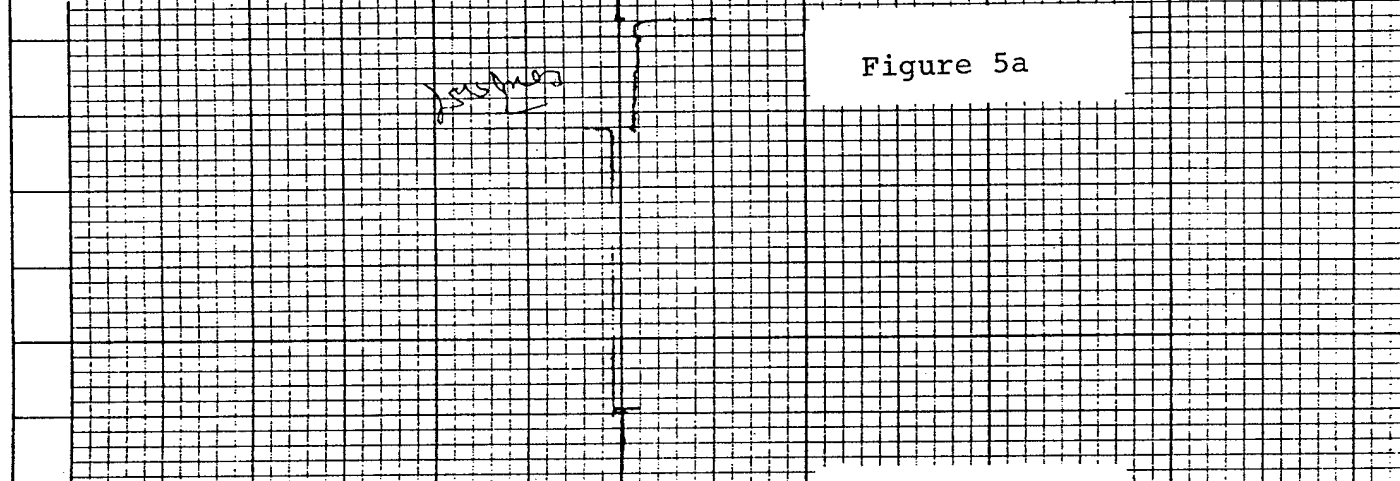


Figure 5b

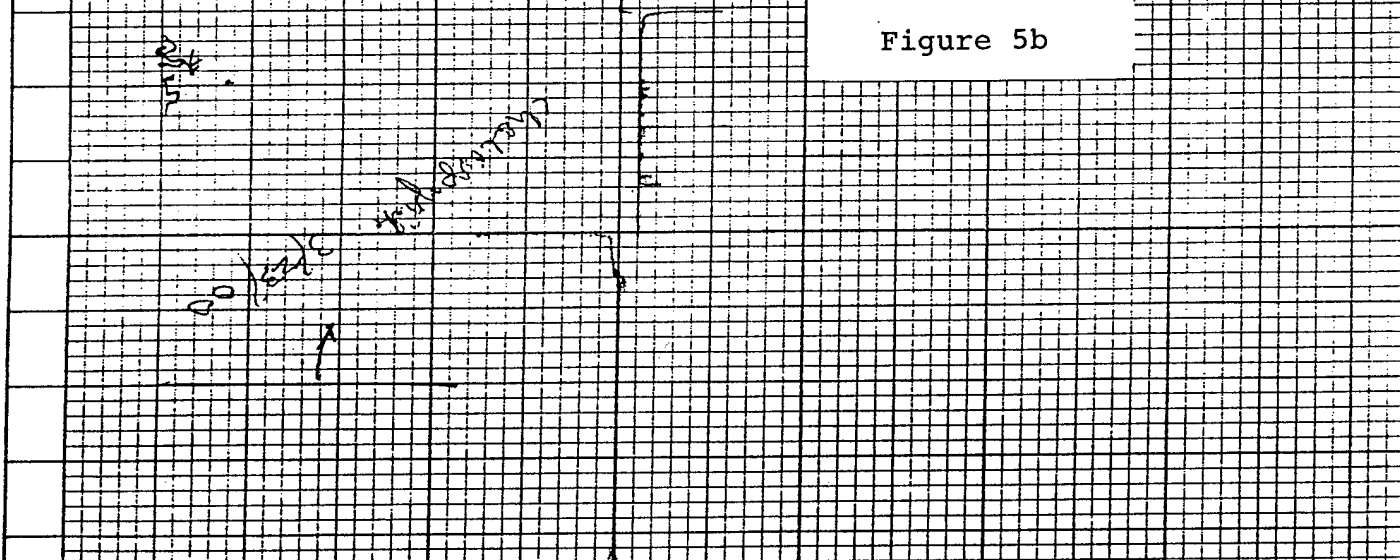


Figure 5c

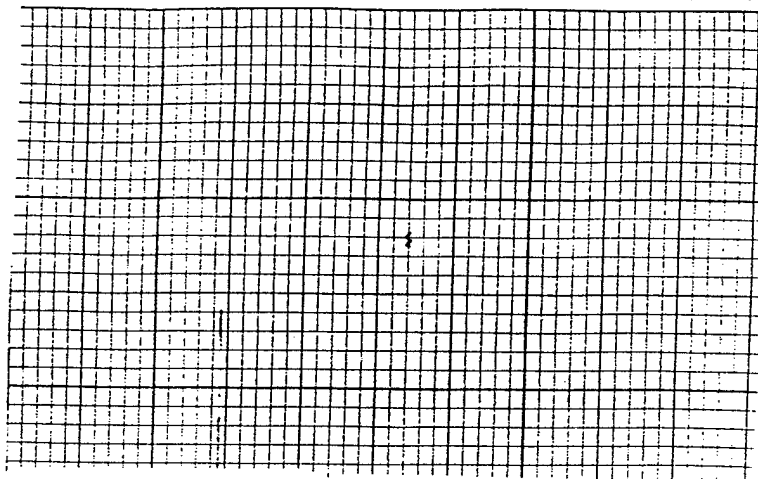
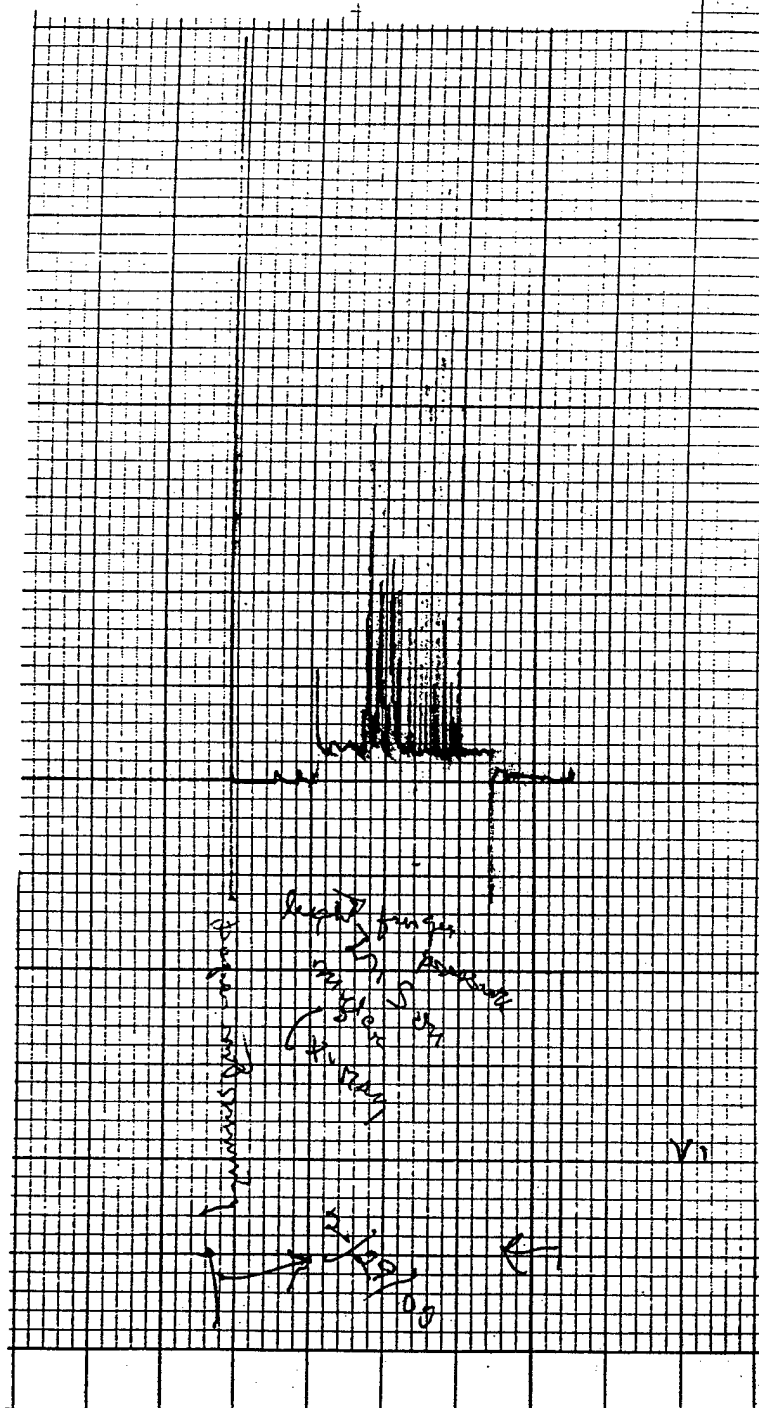


Figure 6a

Figure 6b



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